Nigerian Research Journal of Engineering and Environmental Sciences 6(2) 2021 pp. 706-713
p ISSN: 2635-3342; e ISSN: 2635-3350

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

Original Research Article

Synthesis of Soybean Soapstock Methyl Ester through a Two-Step Transesterification Process

***[1]Mbah, C.G. and [2]Esonye, C.**

[1]Department of Chemical Engineering, Federal Polytechnic, Oko, Anambra State, Nigeria.
[2]Department of Chemical and Petroleum Engineering, Alex Ekwueme Federal University Ndufu Alike Ikwo, Ebonyi State, Nigeria.
*gadoral@yahoo.com

http://doi.org/10.5281/zenodo.5805308

ARTICLE INFORMATION

Article history:
Received 24 Aug, 2021
Revised 08 Oct, 2021
Accepted 18 Oct, 2021
Available online 30 Dec, 2021

Keywords:
Soybean soapstock
Methyl ester
Transesterification
n-hexane
Biodiesel

ABSTRACT

Soybean soapstock (SS) as a lipid-rich by-product produced during vegetable oil refining process, is one of the most promising candidates for biodiesel production because of its easy collection, availability and low cost. In this work, the feasibility of biodiesel production from SS which contains high water and fatty contents was investigated in a two-stage process (esterification followed by transesterification). Sodium hydroxide (NaOH) catalyst, a methanol solvent and n-hexane co-solvent were used. Characterization using gas chromatography (GC) analysis and Fourier transform infrared (FTIR) spectroscopy were carried out to identify the constituent fatty acids and functional groups respectively in the oil and biodiesel produced. The GC results shows that the soybean soapstock though having an unsaturated fatty acid with the highest percentage (linolenic with 32.261%), had a higher total percentage of saturated fatty acids when compared with the unsaturated fatty acids with myristic, stearic and palmitic acids being the more prominent saturated fatty acids with percentages of 15.696%, 15.542% and 14.898% respectively, while the biodiesel had a higher percentage of unsaturated fatty acids with oleic acid (26.045%) and linolenic acid (22.344%) having the highest percentages. Physico-chemical properties of the feedstock and biodiesel showed that the fuel properties of the biodiesel comparing favourably with standards. A biodiesel yield of 96.8wt% was obtained which thus confirms that soybean soapstock was a viable feedstock for the production of biodiesel.

1. INTRODUCTION

Due to the increase in the price of petroleum products and the environmental concerns about air pollution from vehicles, the use of renewable resources as alternative petroleum fuels is gaining growing interest (Marchetti et al., 2007). Biodiesel, defined as an alternative diesel fuel derived from the oils and fats of plants

and animals, has become a fast growing market product during the last few years (Ramadhas et al., 2005). Biodiesel has gained significant attention in recent years because of its renewability and environment-friendliness compared to fossil diesel. Biodiesel has been mainly produced from edible vegetable oils including soybean, palm, and rapeseed oil. Transesterification is by far the most common method to produce biodiesel, and the commercial process is catalytically transesterified by homogeneous acid or base (Semwal et al., 2011).

Since the prices of edible vegetable oils are quite high, many efforts have been devoted to finding cheaper feedstock such as non-edible vegetable oils or waste oils for the biodiesel production (Ayhan et al., 2016). Exploitation of these vegetable oils and animal fats as energy sources plays an important role in our energy, economy and environment system. Refined vegetable oils are glyceride-based materials that can be used for biodiesel production, however their high cost due to competition with food has made them unpopular as feedstocks for biodiesel production. Low-cost oils such as non-edible oils, waste cooking oils and soapstocks can be used as feedstock for biodiesel production (Lin et al., 2011). Non-edible soybean soapstock has been found to be a better raw material for the synthesis of biodiesel, because it is relatively centralized, readily available and reasonably cheap (Moser., 2011). However, such oils usually contain some amounts of water and free fatty acids (FFAs). The FFAs are not converted to esters but soap when homogeneous base catalysts are used (Li and Yan.,2010).

Soybean soapstock (SS), produced during soybean oil refining process, is an important feedstock for biodiesel production because of its availability and reduced cost. SS is generated at a rate of 6% of the volume of the crude oil produced with its price only one-tenth of the refined oil (Wang et al., 2007).

Extensive works to obtain biodiesel from acid oil (acidulated soybean soapstock) have also been carried out by Nakyung (2014). He developed a two-stage process to produce biodiesel from acid oil. In this process, SS was fully saponified by using an excess alkaline catalyst in the first stage. In the second stage, conventional acidulation has been applied to separate high-acid acid oil (HAAO) having over 96% free fatty acid from water and other substances. Park et al. (2008) also investigated the feasibility of biodiesel production from soapstock using a solid acid catalyst. Soapstock was converted to high-acid acid oil by the hydrolysis by potassium hydroxide (KOH) and the acidulation by sulfuric acid. The high cost of acidulation which involves high temperatures and pressure and the high cost of the catalysts involved in the works by Nakyung (2014) and Park et al. (2008) however necessitated the need for an alternative production route. This work will however seek to produce biodiesel through the transesterification of soybean soapstock using n-hexane as a co-solvent to boost biodiesel yield and quality and thus by-passing the high cost of acidulation carried out in previous works.

2. MATERIALS AND METHODS

2.1. Reagents and Equipment

The reagents used were methanol (Sigma-Aldrich), sodium hydroxide (NaOH) flakes, phenolphthalein, sulphuric acid, magnesium trisilicate, sodium sulphate, n-hexane and diethyl ether. Among the equipment used were a centrifuge (used for separation of soapstock from water and impurities), electronic weighing balance (B. Bran Scientific, England), heat drying oven (DHG Series Ocean Med^{+} England), electronic temperature regulation heating mantle (98-I-B Series), HH-S thermostatic water bath (DKS Series; Ningbo Biocotek Scientific Instrument Co. Limited, gas chromatography coupled FID and ECD (for obtaining fatty acid profiles) and buck scientific infra-red spectrophotometer (for characterizing of the samples). All the reagents were of the required analytical standard and obtained from Springboard research laboratories, Awka, Anambra State, Nigeria.

2.2. Sample Collection

Contaminated soybean soapstock was obtained from Sunchi farms, an integrated poultry and feed processing plant in Enugu State, Nigeria. The soybean soapstock was collected in a clean gallon. Prior to use, it was

centrifuged for 7 minutes at 3,000 rpm and 25 ºC. It was separated into three layers after centrifugation. The top layer which is the acid oil (AO), otherwise known as the soapstock was collected for use. The middle and bottom layer which are emulsified materials containing lipids, salts and water were discarded.

2.3. Characterisation of Soybean Soapstock and Biodiesel

The fatty acid composition of the soybean soapstock was analyzed by gas chromatography coupled with mass spectrometer according to AOAC official method (AOAC., 2000). The GC column used was calibrated by injecting methyl ester standards. Good separations were achieved by diluting the samples (n-hexane collected) in a small amount of ethyl acetate. The carrier gas used was hydrogen and its flow rate was regulated at 41.27 ml/mins. The oven temperature was set at 80 ºC before rising at 6 ºC/min to 340 ºC. The identification of peaks was done by comparison of their retention time and mass spectra with mass spectra library (NIST05s LIB) (Fu et al., 2008). The gas chromatography analysis was carried out for both the soybean soapstock and its biodiesel.

2.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis was performed to monitor the functional groups in the soybean soapstock and the biodiesel produced using an FTIR spectrometer (Shimadzu, model No: 3116465).

2.5. Biodiesel Production

Esterification was carried out by mixing equal volume of Soybean soapstock and alcohol (methanol) in a beaker. Sulphuric acid in the ratio of 1:10 to the solution was added, the solution was then heated to 60 ºC for 80 mins. The solution was then separated in a separating funnel. The esterified oil (30 ml) was mixed with methanol and n-hexane in the ratio of 1:3:3 respectively. Sodium hydroxide (NaOH)and catalyst (2%) was added and the mixture stirred at a speed of 300 rpm. The solution was then heated to 55 ºC for 50 mins. After the base transesterification process, the reaction mixture was allowed to settle for 24 hours inside a separating funnel to allow clear separation of biodiesel from glycerol by gravity. The layer on top was the biodiesel while the bottom layer was glycerol. Thereafter, the two layers were separated by settling, using a separating funnel. The biodiesel separation was carried out by decanting as the glycerol was drained off while the biodiesel remained.

2.6. Physico-chemical Analysis

The physico-chemical analysis of the oil was carried out by ASTM (2008) and AOAC (2000) standard methods. The kinematic viscosity was determined by ASTM D-445 method, the density was determined by ASTM D-1298 method and the pour point determination was made using ASTM D-97 method. The flash point of the fuel was determined by ASTM D-93. The cloud point was estimated according to ASTM D-2500 and acid value was measured following the ASTM D-664 method. The refractive index, specific gravity and iodine value were determined using the appropriate AOAC methods (AOAC, 2000). The sulfur content and calorific value were determined according to ASTM D-4294 and ASTM D-246 methods respectively.

3. RESULTS AND DISCUSSION

3.1. Fatty Acid Profile

The fatty acid composition of the biodiesel obtained from the transesterification of soybean soapstock comprises mainly of unsaturated fatty acid with oleic acid having the highest percentage composition of 26% and linolenic acid slightly lower at 22% as seen in Table 1. The characteristics of the biodiesel would tend towards the characteristics exhibited by oleic and linolenic compounds. The ideal mixture of fatty acid composition/ratio for biodiesel has been suggested to be C16:1, C18:1 and C14:0 in the ratio 5:4:1. Such a biodiesel would have the properties of very low oxidative potential (Knothe., 2005: Schenk et al., 2008). Though this ratio is not always realized most of the time, it paints a picture of the ratio of unsaturated to saturated fatty acid profile needed for oxidative stability in a biodiesel fuel. It shows that the unsaturated fatty acid should have a higher ratio to the saturated ones with one of the reasons being that oxidative stability is

influenced by unsaturation (Ramos et al., 2009). This was observed in the soybean soapstock biodiesel as oleic acid (C18:1) with a % concentration of 26.045% had a similar ratio (3:1) with myristic acid (C14:0) with % concentration of 10.15% when compared with the ratio (4:1) suggested by Schenk et al. (2008). It was however observed that the ratio of unsaturated to saturated fatty acids in the feedstock was different from the fatty acid profile of the biodiesel with the saturated fatty acid higher than the unsaturated fatty acid. The oleic acid to Myristic acid ratio of 1:2however does not conform with that suggested by Schenk et al. (2008) (4:1) for good biodiesels. This further proves the ability of transesterification to produce biodiesels through conversion of saturated compounds into unsaturated fatty acids. It was observed that the predominant unsaturated compound in soybean soapstock was linolenic acid while the predominant saturated compounds were stearic acid, myristic acid and palmitic acid as seen in Table 1. The characteristics of the predominant fatty acid in the feedstock is usually reflected on the fatty acid composition of the biodiesel and consequently on the biodiesel physiochemical properties. Unsaturated fatty acids (Oleic and linolenic) recorded the highest composition after transesterification (26.045% and 22.344% respectively). This change in fatty acid composition in soybean soapstock and its biodiesel further confirms that transesterification transforms compounds from saturation to unsaturation.

Table 1: Comparison of soybean soapstock feedstock and biodiesel fatty acid compositions

Component	Name	Soybean soapstock biodiesel concentration (%)	Soybean soapstock concentration (%)
C12	Lauric acid	6.326	5.993
C16	Palmitic acid	17.409	14.898
C18	Stearic acid	7.839	15.542
C18:2	Linoleic acid	9.882	6.148
C18:1	Oleic acid	26.045	9.462
C18:3	Linolenic acid	22.344	32.261
C14	Myristic acid	10.15	15.696

3.2. FTIR Analysis

The FTIR data of the feedstock and biodiesel are shown in Table 2.

Table 2: Table of FTIR spectra of soya bean soap stock oil and biodiesel

S/n	Wavenumber (cm^{-1})		Functional group	Compounds
	biodiesel	Feedstock		
1	755.56	758.72	C-CI	Chloro (Cl symmetric stretch)
2		896.23	C-CI	Chloro (Cl symmetric stretch)
3	1232.69	1091.59	R-O-R	Ether (C-O symmetric stretch)
4	1309.29	1391.49	$H_2C=CH_2$	Ethene (C=C symmetric stretch)
5		1405.13	$H_2C=CH_2$	Ethene (C=C symmetric stretch)
6	1627.61	1619.94	RNH_3	Primary amine (N-H stretch)
7	1833.90	1839.70	RCOO	Cyclic ester (C-O symmetric stretch)
8	1999.50	1949.92	R-S-C≡N	Thiocyanate (S-C-N antisymmetric)
10		2160.35	RC=O	Carbonyl (C-O stretching vibration)
11		2278.51	RC=O	Carbonyl (C-O stretching vibration)
12	2451.62	2642.52	R-C≡N	Nitriles (C-N antisymmetric stretch)
13	2657.43	2877.74	CH_2	Methylene (C-H stretch)
14		2867.88	CH_2	Methylene (C-H stretch)
15	3035.53	3064.81	RCHOH	Primary alcohol (O-H stretch)
16	3175.34	3177.10	RCHOH	Primary alcohol (O-H stretch)
17	3300.53	3318.33	R_2CHOH	Secondary alcohol (O-H stretch)
18	3417.74	3431.59	R_2N	Secondary amine (N-H stretch)
19	3680.02	3649.07	R_3CH0H	Tetiary alcohol (O-H stretch)

The presence of both groups (OH and OR) in the soybean soapstock and biodiesel as seen in Table 2 are complemented by the presence of cyclic ester compounds (RCOO) seen at 1839.703 cm^{-1} for the oil and 1833.90 cm^{-1} for the biodiesel which are the parent compounds needed for esterification and transesterification. The conversion of OH group to OR group is further explained by the absence of carboxylic acid group (RCOOH) in the biodiesel produced which is noticed at peak of 2156.41 cm^{-1} in Table 2. Biodiesel is also confirmed by the presence of an intense band of C=O (carbonyl group) stretching of methyl ester. This can be seen at peaks of 2160.35 cm^{-1} and 2278.519 cm^{-1} in the FTIR spectra of the biodiesel.

3.3. Physico-chemical Properties of Biodiesel

The physico-chemical properties of soybean soapstock biodiesel is presented in Table 3. The acid value of soybean soapstock biodiesel was high (5.5 mgKOH/g) when compared to acid value of other biodiesels. This however is a feature of feedstocks of plant origin when compared to those of animal origin. The high FFA content in these cases could be attributed to age, geographical location and storage condition of the seeds (Esonye et al., 2019). The soybean soapstock having a high acid value of 48.62 mgKOH/g, necessitated a two-step transesterification required to boost biodiesel yield from the oil. A multistep transesterification or blending of the soybean methyl ester with other methyl esters might be required to further bring down the acid value closer to the required standard (0.8 mgKOH/g) as seen in Table 3. This will improve its suitability for application in diesel engines to avoid corrosion of the fuel system. Viscosity which is a measure of fluid resistance to flow is very important in determining optimum handling, storage and operational conditions. The high viscosity in soybean soapstock methyl ester though not desirable, represents a feature of biodiesels from plant sources. It is however important to note that the viscosity of unsaturated fatty acid depends on number and nature of double bonds but less affected by position (Patel 2017).

Table 3: Fuel properties of soybean soapstock biodiesel compared with standards

Physico-chemical properties	Soybean soap stock biodiesel	Standard Limit		Test
		min	max	
Acid Value (mgKOH/g)	5.50	_	0.80	ASTM D664
Specific gravity	0.87	_	0.88	ASTM D6751
Ash content (%)	0.09	_	0.02	ISO 3987
Moisture content (%)	8.08			
Viscosity (Pa.s)	4.10	1.9	6.00	ASTM D445
Calorific value (MJ/Kg)	30.74			
Refractive index	1.4573		1.40	B100
Cloud point (°C)	3.00	-3.0	12.00	ASTM D6751
Pour point (°C)	0.00	-15.0	0.00	ISO 3016
Flash point (°C)	70.00	100.0	170.00	ASTM D93
Saponification value	1.40	_	0.50	ASTM D664
Iodine value (mgI_2/100 g)	63.20	_	130.00	EN 14111
Peroxide value (Meq/kg)	2.80			
Smoke point (°C)	62.00			
Conductivity (µs/cm)	0.00		0.87	ASTM D6751
Sulphur (%)	0.03		0.05	ASTM D6751

The viscosity in the biodiesel however fell within the standard limits as seen in Table 3. Blending with other fuels could however go a long way in solving the high viscosity and density problems associated with the biodiesel. The calorific value of the biodiesel (30,739 kJ/kg) which is usually a reflection of its feedstock (soybean soapstock) falls just short of the standard limit (35,000 kJ/kg) and could also be compensated by blending and proper feedstock refining. The cold flow properties of the methyl esters were assessed using cloud point and pour point. These are important low temperature fuel parameters because solidification of the fuel may cause blockage of the fuel lines and filters leading to fuel starvation, engine starting problems and engine damage due to poor lubrication. The pour point temperature becomes higher as chain length

increases in saturated FAMEs and become lower for unsaturated FAMEs (Knothe, 2005). This was noticed as biodiesel from soybean soapstock having pour point 0 ºC just falls within the upper standard limit. Knothe (2005) however stated that cloud point decreases with increasing double bonds which was highlighted with the low cloud point of soybean soapstock biodiesel realized (3 ºC) when compared to the upper standard limit of 12 ºC owing to the high percentage of branched chain double bonds present in the soybean soapstock biodiesel. Iodine value which is usually a measure of degree of unsaturation should be less than 130 I_2/100g of oil to be suitable as biodiesels because oils having high unsaturation of fatty acids when heated are prone to polymerization of the glycerides causing formation of deposits and thereby compromising oxidative stability (Knothe, 2008). The iodine value of soybean soapstock biodiesel (63.2 mgI_2/100g) was well within the standard limits as seen in Table 3.

The effect of saturation on kinematic viscosity of soybean soapstock methyl ester (SSSME)was highlighted when compared with coconut oil methyl ester (CME), palm kernel oil methyl ester, (PKME), rapeseed oil methyl ester (RME) and soybean oil methyl ester (SME) as seen in Table 4. It was observed that higher saturation reduces kinematic viscosity with PKME and CME having high percentage of saturated fatty acids recording lower kinematic viscosities of 2.9 mm^2/sec and 2.7 mm^2/sec respectively while RME and SME with lower percentage of saturated fatty acids having higher viscosities of 4.5 mm^2/sec and 6.63 mm^2/sec respectively when compared to SSSME with kinematic viscosity of 4.1 mm^2/sec. Saturation was also seen to favor cold flow properties with highly saturated methyl esters such as CME and PKME having lower pour points (-5 ºC) when compared to the pour point of SSSME (0 ºC). Other cold flow parameters such as cold filter plugging point, cloud point (CP), low-temperature filterability test which also determines the cold flow behavior of diesel fuel are also affected by the compositional changes in fatty acids (Nainwal et al., 2015).Unsaturation on the other hand favors higher densities with RME and SME which had the highest percentage of unsaturated fatty acids recording the highest densities as seen in Table 4. The net calorific values of methyl ester fuels are about 15% lower than that of the diesel fuel as seen in Table 4. Comparing the net calorific values in methyl ester fuels, soybean methyl ester had the highest calorific value due to the high calorie content of the feedstock (soybean). CTME, had a low calorific value of 34.2 MJ partly due to its animal origin whose calorie level are naturally lower compared to biodiesels of plant origin. Since less net calorific value make more fuel consumption for combustion, SSSME thus proved to be the better fuel as regards calorific value. The calorific value of the methyl esters could however be brought to par with the diesel fuels through more efficient separation and purification of the feedstock. The densities of methyl ester fuels were generally higher than that of the diesel fuel. The density of SSSME at 870 kg/m^3 falls within the range of the ASTM D 6751 standard limits as seen in Table 3.

Table 4: Comparison of Physicochemical properties of methyl esters with fossil fuel and standards

Physico-chemical properties	SSSME	CTME	CME	PME	PKME	RME	SME	Fossil diesel	Standard min	Standard max
Calorific value (MJ)	30.7	34.2	35.22	36.85	35.61	36.55	38.22	43.12	35	
Density (kg/m^3)	870	842	874	879	877	886	883	826	-	880
Kinematic viscosity (Pas)	4.1	1.52	2.7	4.5	2.9	4.5	4.1	2.5	1.9	6
Pour point (ºC)	0	-9	-5	12.5	-5	-7.5	0	-12.5	-15	0

3.4. Effect of n-Hexane on Biodiesel Production

The transesterification of esterified soybean soapstock with methanol as the only solvent proved to be a problem as poor FAME yield was recorded as seen in FAME yield comparison with and without n-hexane (co-solvent) as seen in Figure 1. This however led to a need to use a co-solvent in the transesterification

reaction. This led to increased FAME yield of up to 96.8%. n-hexane as a co-solvent helped enhance miscibility between the oil and methanol and thus improving FAME yield (Sakthivel et al., 2013).

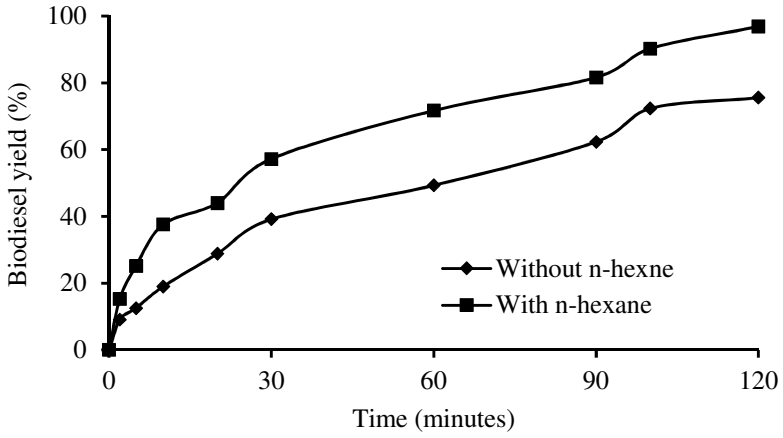

Figure 1: Effect of n-hexane on transesterification of soybean soapstock.

Guo et al. (2012) produced biodiesel from acidified soybean soapstocks by using lignin-derived carbonaceous catalyst. An 80% yield was however a far cry from yield obtained from earlier works. Ma et al. (2017) studied the feasibility of biodiesel production from soybean soapstock containing high water content and fatty matters using an ion exchange resin catalyst. A FAME yield of 98.1% realized in this work was an upgrade on the 91.7 % yield obtained without the use of the catalyst. However, the availability and cost of Amberlyst-15 (the resin catalyst) posed a problem in this process. In an earlier work, Wang et al. (2007) had earlier produced biodiesel from soybean soapstock using sulphuric acid as a catalyst with a biodiesel yield of 97.6% obtained. The high energy demand needed for this process due to the high temperature and pressure requirements however posed a limitation to the commercialization of this process. These cost and feasibility challenges encountered in these alternative routes however makes the use of n-hexane in transesterification of soybean soapstock an attractive prospect for biodiesel production.

4. CONCLUSION

Soybean soapstock can be considered a good and viable feedstock for the production of biodiesel which compared favourably with methyl esters from other feedstocks and fossil fuels. The use of n-hexane as a co-solvent in transesterification of soybean soapstock vastly improved the yield obtained which was low using conventional transesterification procedures. The fatty acid profile of the methyl esters had an effect on the Physico-chemical properties which are the determining factors of the biodiesel quality. The fuel properties of the biodiesel such as viscosity, density, cold flow properties, calorific value and storage stability was also significantly enhanced by transesterification to meet biodiesel standards. A maximum biodiesel yield of 96.8wt% was realized in the course of this work.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Association of Official Analytical Chemists (AOAC) (2000). Official methods of analysis (13th Edition). Association of official analytical chemists, Washington, DC.

ASTM (2008). ASTM Standard specification for diesel fuel oil. In: Annual Book of ASTM Standards, ASTM International: West Conshohocken.

Ayhan, D., Abdullah, B. and Waqar, A. (2016). Biodiesel production from non-edible plant oils. *Energy exploration and exploitation*, 34(2), pp. 290-318.

Esonye, C., Onukwuli, O.D. and Ofoefule, A.U. (2019). Characterization and oxidation modeling of oils from *Prunus amygdalus*, *Dyacrodes edulis* and *Chrysophyllum albidium. Industrial Crops & Products*, 128, pp. 298–307.

Fu, Y. J. Zu. Y. G., Wang. L., Zhang, N. J., Liu. W., Li, S. M. and Zhang, S. (2008). Determination of fatty acid methyl esters in biodiesel produced from yellow corn oil by RP-LC-RID. *Chromatographia*, 67, pp. 9-14.

Guo, F., Xiu, Z.L. and Liang, Z.X. (2012). Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. *Applied Energy*, 10(1), pp. 10-16.

Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology*, 86(10), pp. 1059-1070.

Knothe, G. (2008). "Designer" biodiesel: optimizing fatty ester composition to improve fuel properties. *Energy Fuel*, 22, pp. 1358–1364.

Li, Q and Yan, Y.J. (2010). Production of biodiesel catalyzed by immobilized *Pseudomonas cepacia* lipase from *Sapium sebiferum* oil in micro-aqueous phase. *Applied Energy*, 87, pp. 3148–3154.

Lin, L., Zhou, C., Saritporn, V., Shen, X.Q. and Dong, M.D. (2011). Opportunities and challenges for biodiesel fuel. *Applied Energy*, 88, pp. 1020–31.

Ma, Y., Wang Q., Sun, X., Wu, C. and Gao, Z. (2017). Kinetics studies of biodiesel production from waste cooking oil using $FeCl_3$-modified resin as heterogeneous catalyst. *Renewable Energy*, 107, pp. 522–530.

Marchetti, J. M., Miguel, V. U. and Errazu, A. F. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews*, 11, pp. 1300-1311.

Moser, B.R. (2011). *Biodiesel production, properties, and feedstocks.* In: Tomes, D.,

Lakshmanan, P., Songstad, D., (Eds). Global impact on renewable energy, production agriculture, and technological advancements. New York: Springer. pp. 285–347.

Nainwal, S., Sharma, N., Sharma, A .and Jain, S. (2015). Cold flow properties improvement of *Jatropha curcas* biodiesel and waste cooking oil biodiesel using winterization and blending. *Energy*, 89, pp. 702–707.

Nakyung, C. (2014). Production of biodiesel from acid oil via a two-step enzymatic transesterification. *Energy Conversion and Management*, 88, pp. 60-65.

Park, J.Y., Kim, D.K., Wang, Z.M., Lu, P., Park S.C. and Lee J.S. (2008). Production and characterization of biodiesel from tung oil. *Applied. Biochemistry and Biotechnology*, 148, pp. 109-117.

Patel, V. (2017). Assessment of fuel properties on the basis of fatty acid profiles of oleaginous yeast for potential biodiesel production. *Renewable and Sustainable Energy Reviews*, 77, pp. 604–616.

Ramadhas, A. S., Jayaraj, S.and Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel*, 84(4), pp. 335-340.

Ramos, M. J., Fernandez, C. M., Casas, A., Rodriguez, L. and Perez, A. (2009). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, 100(1), pp.261-268.

Sakthivel, S., Halder, S. and Gupta, P.D. (2013). Influence of co-solvent on the production of biodiesel in batch and continuous process. *International journal of green energy*, 10(8), pp.876-884.

Schenk, P.M., Thomas-Hall, S. R., Stephens, E., Marx, U. C., Mussgnug, J. H., Posten, C., Kruse, O. and Hankamer, B. (2008). Second generation biofuels: High-efficiency for bio- diesel production. *Bioenergy Research*, 1(1), pp. 20-43.

Semwal, S., Arora, A.K and Badoni, R. P. (2011). Biodiesel production using heterogeneous catalysts. *Bioresource Technology*, 102(3), pp. 2151–2161.

Tat, M.E. and Van Garpen, J.H. (2003). Measurement of biodiesel speed of sound and its impact on injection timing. *National Renewable Energy Laboratory series*, 5(10), pp. 314-362.

Wang, Z. M., Lee, J. S., Park, J. Y., Wu, C. Z. and Yuan, Z. H. (2007). Novel biodiesel production technology from soybean soapstock. *Korean Journal of Chemical Engineering*, 24(6), pp. 1027-1030.